Evolution of superconducting order in $Pr(Os_{1-x}Ru_x)_4Sb_{12}$

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We report measurements of the magnetic penetration depth λ in single crystals of $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ down to 0.1 K. Both λ and superfluid density ρ_s exhibit an exponential behavior for the $x \geq 0.4$ samples, going from weak (x=0.4,0.6), to moderate, coupling (x=0.8). For the $x \leq 0.2$ samples, both λ and ρ_s vary as T^2 at low temperatures, but ρ_s is s-wave-like at intermediate to high temperatures. Our data are consistent with a three-phase scenario, where a fully-gapped phase at T_{c1} undergoes two transitions: first to an unconventional phase at $T_{c2} \lesssim T_{c1}$, then to a nodal low-T phase at $T_{c3} < T_{c2}$, for small values of x.

The recent discovery [1, 2] of the heavy Fermion (HF) skutterudite superconductor (SC) $PrOs_4Sb_{12}$ has attracted much interest due to its differences with the other HFSC. Early work suggested that the ninefold degenerate $J = 4$ Hund's rule multiplet of Pr is split by the cubic crystal electric field, such that its ground state is a *nonmagnetic* Γ_3 doublet, separated from the first excited state Γ_5 by ~ 10 K. Hence its HF behavior, and consequently the origin of its superconductivity, might be attributed to the interaction between the electric quadrupolar moments of Pr^{3+} and the conduction electrons [1]. More recent results appear to rule this mechanism out, giving strong evidence for a singlet Γ_1 ground state with a Γ_5 triplet state at a slightly higher energy [3, 4]. In this scheme, aspherical Coulomb scattering [4] and spin-fluctuation scattering [5] have been proposed as mechanisms leading to superconductivity

Surprisingly, replacement of Os by Ru, i.e. in $PrRu_4Sb_{12}$, yields a superconductor with $T_c \approx 1.25$ K [6] and significantly different properties. The effective mass of the heavy electrons calculated from de Haas-van Alphen (dHvA) and specific-heat measurements [1, 7] show that, while $PrOs_4Sb_{12}$ is clearly a HF material, $PrRu_4Sb_{12}$ is at most, a marginal HF. Various experimental results suggest that these two materials have different order-parameter symmetry. Firstly, there is no Hebel-Slichter peak in the nuclear quadrupole resonance (NQR) data [8] for $PrOs_4Sb_{12}$, while a distinct coherence peak was seen [9] in the Sb-NQR $1/T_1$ data for $PrRu_4Sb_{12}$. Secondly, the low-temperature power-law behavior seen in specific heat [1] and penetration depth [10], and the angular variation of thermal conductivity [11], suggest the presence of nodes in the order parameter of $PrOs_4Sb_{12}$. Specifically, Refs. 10 and 11 reveal the presence of *point* nodes on the Fermi surface (FS). For $PrRu_4Sb_{12}$, however, exponential low-temperature behavior was seen in $1/T_1$ [9] and penetration depth [12] data. The latter data were fit with an isotropic zero-temperature gap of magnitude $\Delta(0)=1.9k_BT_c$, showing that $PrRu_4Sb_{12}$ is a moderate-coupling superconductor. Thirdly, muon spin rotation (μSR) experiments on $PrOs_4Sb_{12}$ reveal the spontaneous appearance of static internal magnetic fields below T_c, providing evidence that the superconducting state is a time-reversal-symmetry-breaking (TRSB) state [13]. Such experiments have not been performed on $PrRu_4Sb_{12}$.

It is puzzling that the substitution of Ru for Os (same column in the periodic table) causes $PrRu_4Sb_{12}$ to differ in so many respects from $PrOs_4Sb_{12}$, particularly if symmetry of the superconducting gap varies as we go from Os to Ru. Recently, Frederick *et al.* performed x-ray powder diffraction, magnetic susceptibility and electrical resistivity measurements [14] on single crystals of $Pr(Os_{1-x}Ru_x)_4Sb_{12}$. They found a smooth evolution of the lattice constant and T_c with x, albeit with a deep minimum (0.75 K) in T_c at x=0.6, and an increased splitting between the ground and excited states of the Pr ion. On the other hand, one still has to contend with measurements [10, 11, 13, 15] that indicate point-node gap structure, TRSB and a double superconducting transition $T_{c2} \lesssim T_c$ [14] in $PrOs_4Sb_{12}$, none of which are seen for $x>0$. We report here a complementary study of $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ using the penetration depth.

A recent paper [16] observed an unexpected enhancement of the lower critical field $H_{c1}(T)$ and the critical current $I_c(T)$ deep in the superconducting state below $T \approx 0.6$ K ($T/T_c \approx 0.3$) in $PrOs_4Sb_{12}$. They speculate that this reflects a transition into another superconducting phase that occurs below $T_{c3} \approx 0.6$ K, and may explain anomalies in other measurements, such as the levelling off of Sb-NQR $1/T_1$ below 0.6 K [9], the small downturn of penetration depth below 0.62 K and its deviation from point-node-T^2-behavior above $\sim$0.6 K [10].

In this Letter, we present high-precision measurements of the penetration depth $\lambda(T)$ of $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ (x=0.1,0.2,0.4,0.6,0.8) at temperatures down to $\sim$0.1 K using the same experimental conditions as for $PrOs_4Sb_{12}$ and $PrRu_4Sb_{12}$ [10, 12]. For the $x \geq 0.4$ samples, both $\lambda(T)$ and superfluid density $\rho_s(T)$ exhibit exponential behavior at low temperatures, supporting the presence of

an isotropic superconducting gap on the FS. The $\rho_s(T)$ data agree with the theoretical curve over the entire temperature range. The values of $\Delta(0)$ used in the fits suggest an increase in coupling strength from weak-coupling (x=0.4,0.6) to moderate coupling (x=0.8). On the other hand, the $x\leq$0.2 samples exhibit a low-T power law, implying the existence of low-lying excitations. However, the ρ_s data fit a fully-gapped theoretical curve from intermediate temperatures up to T_c, but not curves based on a superconducting gap with line or point nodes. This is consistent with the scenario depicted by Cichorek *et al.* [16], where for the $x\leq$0.2-samples, the fully-gapped high-T phase undergoes a transition into a nodal low-T phase below $T_{c3}(x)$. As x increases, the low-T phase is suppressed (T_{c3} decreases) such that for the $x \geq 0.4$-samples, T_{c3} falls below the base temperature of our experiment, and we are left with a fully-gapped phase over our entire experimental temperature range. Taken together with other data, we suggest that, in addition to the two phases at T_{c1} and T_{c2}, there is a third superconducting phase at T_{c3} that exhibits point nodes.

The single crystal samples were grown by Sb self-flux method [6]. The observation of dHvA effect both in $PrOs_4Sb_{12}$ and $PrRu_4Sb_{12}$ could be an indirect evidence of high quality of these samples grown in the same manner. Measurements were performed utilizing a 21-MHz tunnel diode oscillator [17] with a noise level of 2 parts in 10^9 and low drift. The magnitude of the ac field is estimated to be less than 40 mOe. The sample was mounted, using a small amount of GE varnish, on a single crystal sapphire rod. The other end of the rod is thermally connected to the mixing chamber of an Oxford Kelvinox 25 dilution refrigerator. The sample temperature is monitored using a calibrated RuO_2 resistor at low temperatures (T_{base}–1.3 K) and a calibrated Cernox thermometer at higher temperatures (1.2 K–1.8 K).

The deviation $\Delta\lambda(T)$=$\lambda(T)$–λ(0.1 K) is proportional to the change in resonant frequency $\Delta f(T)$ of the oscillator, with the proportionality factor G dependent on sample and coil geometries. We determine G for a pure Al single crystal by fitting the Al data to extreme nonlocal expressions and then adjust for relative sample dimensions [18]. Testing this approach on a single crystal of Pb, we found good agreement with conventional BCS expressions. The value of G obtained this way has an uncertainty of ±10% because our samples have a rectangular, rather than square, basal area [19].

We first discuss the $x \geq 0.4$ samples. Figure 1 (◯) shows $\Delta\lambda(T)$ for the three samples (x=0.4,0.6,0.8) as a function of temperature in the low-temperature region. The insets show $\Delta\lambda(T)$ for the entire temperature range. The onset of the superconducting transitions T_c^* are 0.81 K (x=0.6) and 0.88 K (x=0.8). These values are consistent with those of Ref. 14. We could not obtain T_c^* for the x=0.4 sample as the ac losses were so large that oscillation was lost before T_c was reached; its large

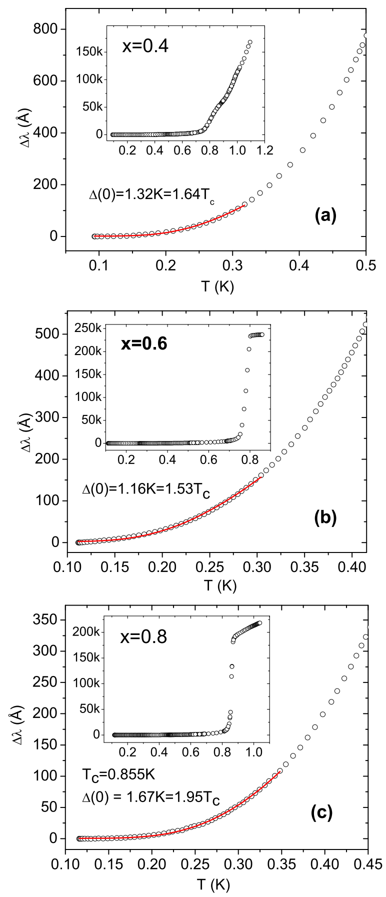

FIG. 1: (◯) Low-temperature dependence of $\Delta\lambda(T)$ for (a) x=0.4, (b) x=0.6, and (c) x=0.8. Lines: fits to BCS low-T expression from T_{base} to $0.4T_c$. The parameters of the fits are described in the text. Insets show $\Delta\lambda(T)$ over the full temperature range.

transition width is also consistent with the ac susceptibility data of Frederick *et al.* [14], though the origin is unknown. The values of T_c, determined from the point where the experimental superfluid density almost vanishes and fit the theoretical curves (described later), are 0.8 K (x=0.4), 0.76 K (x=0.6) and 0.86 K (x=0.8).

For all three samples the data points flatten out below $0.3T_c$, implying activated behavior in this temperature range. We fit these data to the BCS low-temperature expression in the clean and local limit, from T_{base} (~0.1 K) to $0.4T_c$, using the expression $\Delta\lambda(T)\propto\sqrt{\pi\Delta(0)/2k_BT}\exp(-\Delta(0)/k_BT)$, with the proportionality constant and $\Delta(0)$ as parameters. The best fits (solid lines) are obtained when $\Delta(0)/k_BT_c$=1.64 (x=0.4), 1.53 (x=0.6) and 1.95 (x=0.8). This implies that the x=0.4 and 0.6 samples are weak-coupling, while the x=0.8 sample is a moderate-coupling, superconductor. The x=0.8 result is consistent with that for $PrRu_4Sb_{12}$ (x=1).

Sample x	0	0.1	0.2	0.4	0.6	0.8	1.0
$\Delta(0)/k_BT_c$	2.6	1.76	1.76	1.76	1.76	1.95	1.90
$\Delta C/C$	3.0	1.43	1.43	1.43	1.43	2.04	1.87
$\lambda(0)$ (nm)	344	320	380	340	380	400	290

TABLE I: Parameters used to calculate curves in Figs. 2 and 3. Values for x=0 and x=1 are included for comparison.

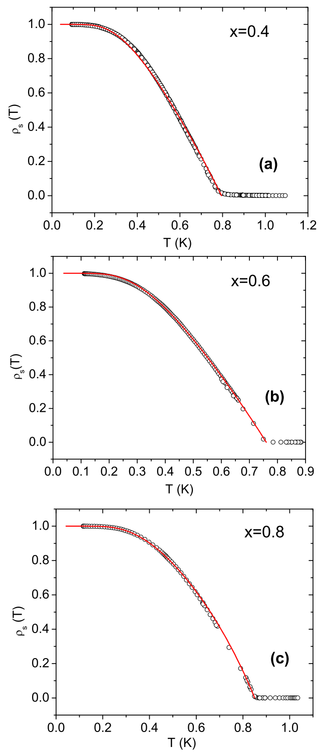

FIG. 2: (◯) Superfluid density $\rho_s(T) = [\lambda^2(0)/\lambda^2(T)]$ calculated from $\Delta\lambda(T)$ data in Fig. 1, for (a) x=0.4, (b) x=0.6, and (c) x=0.8. Lines: Theoretical $\rho_s(T)$ with parameters $\Delta(0)/k_BT_c$ and $\Delta C/\gamma T_c$ mentioned in the text.

To extract the superfluid density ρ_s from our data, we need to know $\lambda(0)$. Absent published data on $\lambda(0)$, we assume that it lies in the vicinity of 344 nm (for $PrOs_4Sb_{12}$) [20] and 290 nm (for $PrRu_4Sb_{12}$) [12]. We compute ρ_s for an isotropic s-wave superconductor in the clean and local limits using $\rho_s = 1 + 2\int_0^\infty \frac{\partial f}{\partial E} d\varepsilon$, where $f = [\exp(E/k_BT)+1]^{-1}$ is the Fermi function, and $E = [\varepsilon^2 + \Delta(T)^2]^{1/2}$ is the quasiparticle energy. The temperature-dependence of $\Delta(T)$ can be obtained by using [21] $\Delta(T)=\delta_{sc}k_BT_c \tanh\{(\pi/\delta_{sc})\sqrt{(2/3)[(\Delta C)/C][(T_c/T)-1]}\}$, where $\delta_{sc}\equiv\Delta(0)/k_BT_c$ is the only variable parameter. The specific heat jump $\Delta C/C$ can be obtained from $\Delta(0)/k_BT_c$ using strong-coupling equations [22, 23] .

Fig. 2 shows the experimental(◯) and calculated (solid line) values of ρ_s as a function of temperature for the $x \geq 0.4$ samples. The theoretical curves fit the data very well using the parameters shown in Table I. Fitted values for $\lambda(0)$ are reasonable, considering the uncertainty in obtaining the calibration factor G.

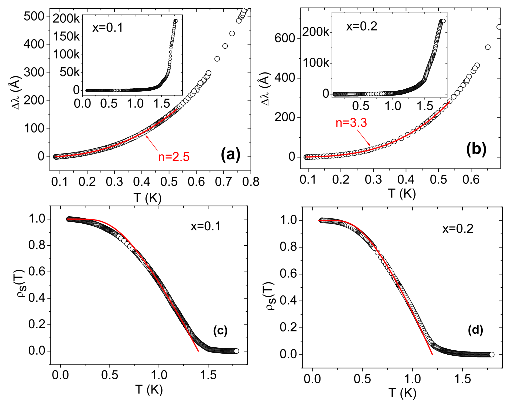

FIG. 3: (◯) Low-temperature $\Delta\lambda(T)$ for (a) x=0.1 and (b) x=0.2. Lines: fits to $\Delta\lambda(T)$=A+BT^n from 0.1 K to 0.53 K. Insets show $\Delta\lambda(T)$ over the full temperature range. (◯) Superfluid density $\rho_s(T)$ calculated from $\Delta\lambda(T)$ data for (c) x=0.1 and (d) x=0.2. Lines: Theoretical $\rho_s(T)$ with weak-coupling parameters. Note the deviation of data from the theoretical curve at low temperatures is more pronounced for x=0.1 than for x=0.2.

We now turn to the x≤0.2-samples. Figs. 3a and 3b show $\Delta\lambda(T)$ in the low-temperature region. The insets show $\Delta\lambda(T)$ for the entire temperature range. T_c^* is measured to be 1.76 K (x=0.1) and 1.77 K (x=0.2), while T_c is 1.4 K (x=0.1) and 1.2 K (x=0.2). A fit of the low-temperature data (up to 0.53 K≈$0.3T_c^*$) to a variable power law $\Delta\lambda(T)$=A+BT^n yields n=2.5 (x=0.1) and 3.3 (x=0.2), indicative of low-lying excitations and incompatible with an isotropic gap.

Figs. 3c and 3d show the experimental (◯) values of $\rho_s(T)$. The solid lines represents the theoretical curve based on an isotropic weak-coupling gap as in Table I. Note that the data do not agree with the theoretical curve at low temperatures, but agree from intermediate temperatures up to near T_c. The deviation of data from the theoretical curve at low temperatures is more pronounced for x=0.1 than for x=0.2. This is consistent with the scenario depicted by Cichorek *et al.* [16], where for these low-x samples, the fully-gapped high-T phase undergoes a transition into a nodal low-T phase below $T_{c3}(x)$. Our data also agree with the theory of Hotta [5], which predicts that when the Γ_1-Γ_5 spacing increases (observed as x is increased from 0 to 1 [14], and for x=1 [6]), superconductivity changes from unconventional to conventional. We assume that this nodal phase is a *point-node* one, consistent with Refs. 10, 11, and so $\Delta\lambda \propto T^2$ in this phase. Consequently, we plot $\Delta\lambda(T)$ vs T^2, shown in Fig. 4a and 4b. $T_{c3}(x)$ is determined from the temperature where the data deviate from linearity, from which we obtain $T_{c3}(x$=0.1)≈0.32±0.02 K and $T_{c3}(x$=0.2)=0.15±0.02 K. Together with $T_{c3}(x$=0)≈0.61±0.01 K deduced in Ref. 16 and 10, we plot T_{c3} vs x in Fig. 4c. We see that T_{c3}

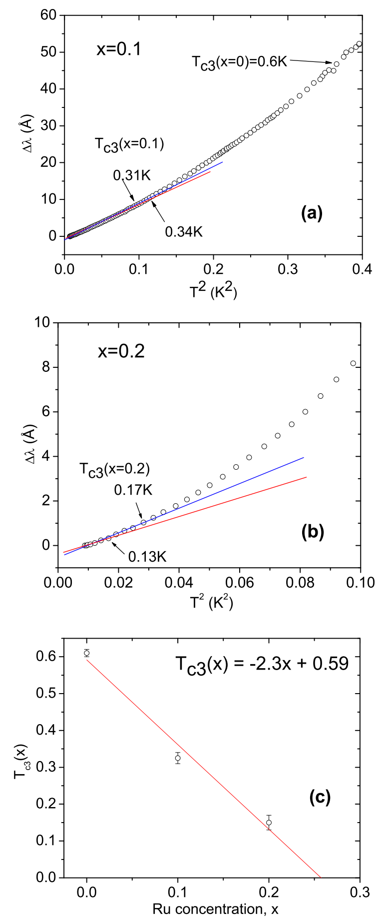

FIG. 4: (◯) Low-temperature $\Delta\lambda(T)$ vs T^2 for (a) x=0.1 and (b) x=0.2. The solid lines are visual aids to determining the range of linear fit. T_{c3} is defined to be the temperature where $\Delta\lambda(T)$ starts to depart from T^2-behavior. (c) (◯) $T_{c3}(x)$ for x=0,0.1,0.2. Line: Best linear fit to the three data points. Note that the line extrapolates to zero near x=0.26.

varies linearly with x. Extrapolating the best-fit line yields $T_{c3}\approx 0$ when $x\approx 0.26$. This implies that the low-T nodal phase disappears, perhaps at a quantum critical point, when $x \gtrsim 0.3$, i.e. one only sees a fully-gapped behavior over the whole temperature range, agreeing with our $x\geq 0.4$ data sets.

The continuity across the series of the first superconducting transition, that we label T_{c1}, and the BCS-like behavior of ρ_s over much of the T-x plane, suggest that conventional phonon-mediated superconductivity prevails. Nonetheless, there is ample evidence for a second superconducting transition at T_{c2} at x=0 below which unconventional superconductivity appears. Specific heat measurements on $\mathrm{Pr}_{1-y}\mathrm{La}_y\mathrm{Os}_4\mathrm{Sb}_{12}$ [24] showed that the second superconducting transition at T_{c2} disappears between y=0.05 and 0.1, leaving conventional superconductivity for larger values of y. Figs. 1a, 3a and 3b show some changes in curvature in $\Delta\lambda$ close to T_c^* for the x=0.1, 0.2 and 0.4 samples that could be indicative of T_{c2}, but which are not reproducible from sample to sample. As noted in the introductory paragraph, two mechanisms — spin-fluctuation and aspherical Coulomb scattering—have been proposed to explain the heavy-fermion behavior and superconducting properties of the x=0 skutterudite. One possibility is that the spin-fluctuation mechanism is active at high temperatures where the Γ_5 state is thermally populated on the Os-rich end of the phase diagram, but is suppressed by decreasing temperature or as Ru doping increases the Γ_1-Γ_5 splitting. Aspherical Coulomb scattering may remain important at lower temperatures and at larger values of x. Our data, when considered together with other data and theory, suggest *three* different superconducting phases: phonon-driven (conventional) across the series at the upper transition T_{c1}, but with spin-fluctuation and aspherical Coulomb scattering at the Os end giving rise to transitions to unconventional phases at T_{c2} and T_{c3}.

In conclusion, we report measurements of the magnetic penetration depth λ in single crystals of $\mathrm{Pr(Os}_{1-x}\mathrm{Ru}_x)_4\mathrm{Sb}_{12}$ down to ∼0.1 K. Both λ and superfluid density ρ_s exhibit an exponential behavior for the $x\geq 0.4$ samples, going from weak-coupling (x=0.4,0.6) to moderate-coupling (x=0.8). For the $x\leq 0.2$ samples, both λ and ρ_s vary as T^2 at low temperatures, but ρ_s is s-wave-like at intermediate to high temperatures. Our data are consistent with a three-phase scenario, where a fully-gapped phase at T_{c1} undergoes a transition to an unconventional phase at $T_{c2}\approx T_{c1}$, then to a nodal low-T phase at T_{c3} for small values of x. The x-dependence of T_{c3} suggests that the low-T phase disappears near x=0.3.

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